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The Origin of Hierarchical Structure Formation in Highly Grafted Symmetric Supramolecular Double-Comb Diblock Copolymers

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and Katja Loos*

Involving supramolecular chemistry in self-assembling block copolymer systems enables design of complex macromolecular architectures that, in turn, could lead to complex phase behavior. It is an elegant route, as complicated and sensitive synthesis techniques can be avoided. Highly grafted double-comb diblock copolymers based on symmetric double hydrogen bond accepting poly(4-vinylpyridine)-*block*-poly(*N*-acryloylpiperidine) diblock copolymers and donating 3-nonadecylphenol amphiphiles are realized and studied systematically by changing the molecular weight of the copolymer. Double perpendicular lamellae-*in*-lamellae are formed in all complexes, independent of the copolymer molecular weight. Temperature-resolved measurements demonstrate that the supramolecular nature and ability to crystallize are responsible for the formation of such multiblock-like structures. Because of these driving forces and severe plasticization of the complexes in the liquid crystalline state, this supramolecular approach can be useful for steering self-assembly of both low- and high-molecular-weight block copolymer systems.

As a result of their direct covalent linkage and inability to mix, block copolymers are known to spontaneously form ordered nanometer-sized structures with the type being predominantly dependent on their composition and architecture.^[1,2] The total molecular weight generally determines the size of this structure, whereas the minimum size that can be achieved with a certain monomer couple relies on the Flory–Huggins interaction parameter χ .^[3,4] The ability of large block copolymer morphologies (>100 nm) to interact with the visible light makes them highly attractive for applications in which a solution processable material is desired.^[5] Such fully polymeric

photonic crystals (i.e., materials with a periodically varying refractive index) are therefore particularly interesting for antireflective coatings and pigment-free paints or fabrics.^[6] Both the preparation and self-assembly of high-molecular-weight linear block copolymers are however an extremely challenging task, since complex synthesis strategies are required and their high melt viscosity obstructs the ability to reach an ordered equilibrium morphology. Molecular weights of over 400 kg mol⁻¹ are no exception.^[7,8] A very clever solution involves the use of bottlebrush (or double-comb) block copolymers that are often prepared through ring-opening metathesis polymerization (ROMP) of macromonomers.^[9] Their high entanglement molecular weight enables rapid formation of ordered structures with periodicities of over 200 nm, whereas the

extended worm-like conformation leads to almost linear scaling of the long period with the backbone length.^[10] Several research groups indeed successfully utilized these properties for the design of block copolymer-based photonic crystals.^[11–13]

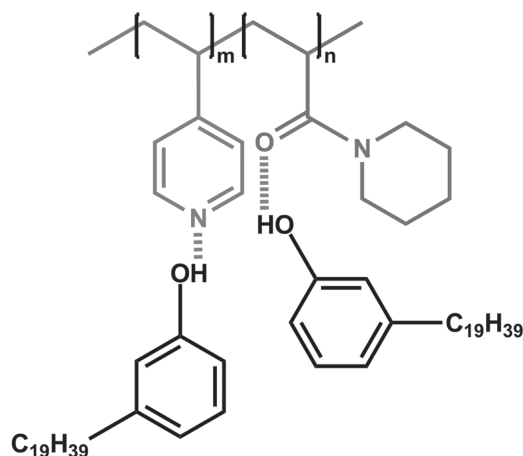
However, the additional synthetic steps as opposed to conventional linear block copolymers are a major drawback of this approach. Switching to supramolecular chemistry allows preparation of comb-shaped polymers by simply combining regular linear polymers and surface active molecules.^[14] Multiple systems have been investigated during the past decades, including ionic,^[15,16] halogen-bonded,^[17] and hydrogen-bonded copolymers.^[18] Still poly(4-vinylpyridine)(*n*-alkylphenol)_x-based supramolecules are among the most studied comb-shaped copolymers (*x* represents the surfactant-to-monomer ratio).^[19] Besides reduction of poly(4-vinylpyridine) (P4VP)'s glass transition temperature upon addition of small amounts of 3-pentadecylphenol (3-PDP) (its *T_g* is already decreased by 100 °C for *x* = 0.5),^[20] simultaneous self-assembly of the diblock (i.e., P4VP(3-PDP)/PS) and comb block (i.e., P4VP/3-PDP) led to hierarchical structure formation in polystyrene-containing poly(4-vinylpyridine)(3-pentadecylphenol)_x-*b*-polystyrene (P4VP(3-PDP)_x-*b*-PS) comb-coil diblock copolymers.^[21]

Recently, our group reported hierarchical self-assembly of bottlebrush-like supramolecular double-comb diblock copolymers by starting from a double hydrogen bond accepting diblock

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Scheme 1. Schematic representation of a P4PA(3-NDP)_{1.0} supramolecular double-comb diblock copolymer.

copolymer.^[22] Besides spontaneous formation of double perpendicular lamellae-*in-lamellae*, facile adjustment of the grafting density in a symmetric [poly(4-vinylpyridine)-*block*-poly(*N*-acryloyl-piperidine)](3-nonadecylphenol)_x ([P4VP-*b*-PAPI](3-NDP)_x, or P4PA(3-NDP)_x in short) double-comb resulted in double parallel lamellae-*in-lamellae* or cylinders-*in-lamellae* for lower comb densities.^[23] On the other hand, varying the parent diblock copolymer molecular weight while keeping *x* fixed at 0.5 caused the complexes to self-assemble into fascinating double parallel lamellar morphologies.^[24] As opposed to these low-*x* complexes, the ability of the highly grafted supramolecule (*x* = 1.0) to form an ordered perpendicularly oriented structure is quite surprising, especially when regarding its low block copolymer concentration (≈25 wt%). Motivated by this intriguing behavior, we have studied the self-assembly of a range of such highly grafted symmetric supramolecular P4PA(3-NDP)_{1.0} double-comb diblock copolymers (Scheme 1) in order to gain better insight into the mechanism behind the formation of

lamellar-*in-lamellar* morphologies. Structure formation occurs at both small and large length scales, making our approach attractive for multiple applications.

Five P4PAy-*z* diblock copolymers (*y* is the molecular weight in kg mol⁻¹, *z* is the weight percentage of P4VP) with a symmetric composition (i.e., $f_{P4VP} \approx 0.5$) were prepared via reversible addition-fragmentation chain transfer (RAFT) polymerization using the method^[25] and conditions^[24] as described previously. Molecular weights ranged from 30.5 up to 272 kg mol⁻¹ and polydispersity indices never exceeded a value of 1.3. Detailed molecular weight characteristics can be found in Table S1 (Supporting Information). Transmission electron micrographs of stained P4PA sections as displayed in Figure 1 demonstrate all neat diblock copolymers to have self-assembled into the expected lamellar morphology. Small-angle X-ray scattering (SAXS) profiles enabled estimation of their long period by using the first-order scattering maxima (Figure 1f). Sizes were calculated to be 22.6 nm for the diblock of lowest molecular weight (P4PA31k-47) and 132 nm for the highest (P4PA272k-51; Table S1, Supporting Information).

Although the previously found perpendicular orientation^[23] of the small 3-NDP lamellae with respect to the large P4PA lamellae was in excellent agreement with our theoretical, but highly simplified, all-covalent analysis,^[26] it is exciting to see that despite the low concentration of P4PA (about 25 wt%), such a complex was still able to assemble into an ordered morphology at room temperature. By preparation of additional stoichiometric P4PA(3-NDP)_{1.0} complexes using these five symmetric P4PA diblock copolymers and studying those by several temperature-resolved techniques, we will present a more detailed description of the mechanism that drives the self-assembly of these intriguing supramolecules.

The thermal behavior of the complexes, that was obtained by differential scanning calorimetry (DSC), is demonstrated in Figure 2. Similar trends can be observed in all five P4PA(3-NDP)_{1.0} complexes: upon heating, each complex contains two melting events, origination from melting of the 3-NDP combs

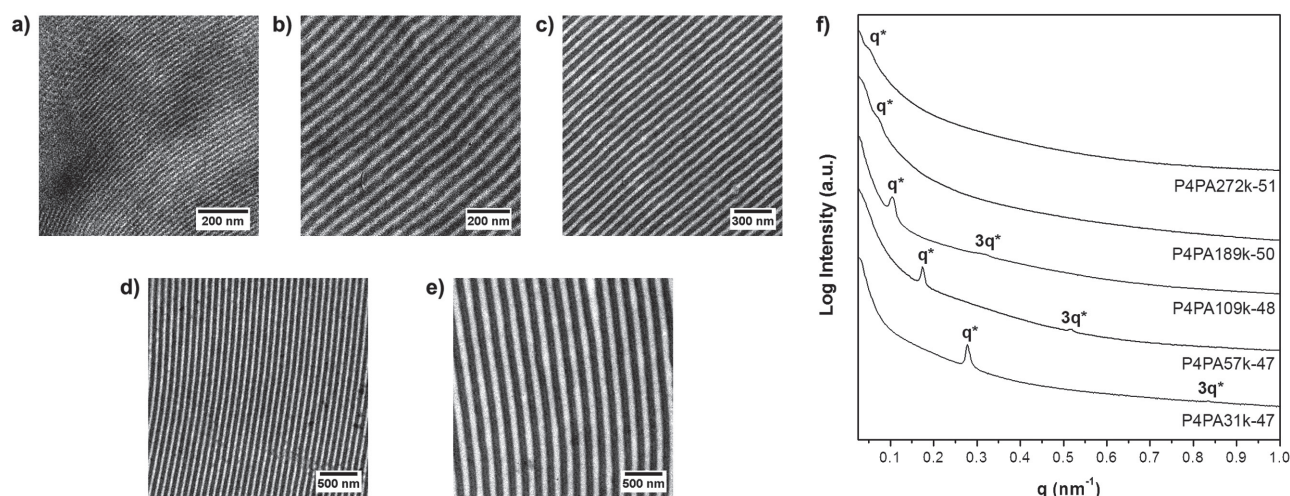


Figure 1. Bright field TEM images of iodine-vapor-treated P4PA diblock copolymers (P4VP domains appear dark). a) P4PA31k-47, b) P4PA57k-47, c) P4PA109k-48, d) P4PA189k-50, and e) P4PA272k-51. f) Room temperature SAXS patterns of the neat P4PA diblock copolymers. First-order scattering maxima (q^*) were used for determination of the long period *d*.

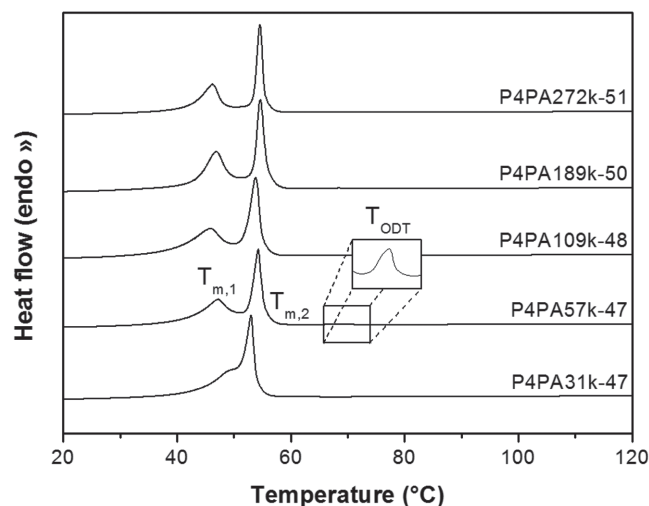


Figure 2. DSC thermograms of P4PA(3-NDP)_{1,0} supramolecular double-comb diblock copolymers. $T_{m,1}$ is consistent with PAPI(3-NDP) and both $T_{m,2}$ and T_{ODT} with P4VP(3-NDP).

on the PAPI ($T_{m,1}$, 45 °C) and P4VP side ($T_{m,2}$, 55 °C), and a single P4VP(3-NDP) liquid crystalline to disordered transition around 70 °C (T_{ODT}).

Analysis of iodine-stained sections by transmission electron microscopy (TEM) indeed showed all complexes to have self-assembled on the block copolymer level at room temperature, whereas a small, perpendicular lamellar structure can be observed within the dark, stained P4VP layers (**Figure 3a–e**). Structures were found to cover large areas (**Figure S1**, Supporting Information). The appearance of large lamellae suggests approximately equal distribution of 3-NDP over both phases and is supported by the presence of two distinct melting points in DSC, that are identical to the transitions observed in the equimolar homopolymer complexes.^[23] Small lamellae within the bright PAPI layers can simply not be observed due to the applied staining technique.

TEM micrographs of unstained sections indeed show large regions containing small lamellae, implying the formation of a small structure inside PAPI as well (**Figure 3f–j**). Although the low contrast prevents direct imaging of both copolymer phases, in certain cases kink bands and/or contrast difference between domains could indicate the presence of diblock interfaces, providing indirect evidence for the formation of double perpendicular lamellar-*in*-lamellar morphologies (**Scheme 2a**). Moreover, in certain cases, Fourier transformations of images recorded at a lower magnification (**Figure S2**, Supporting Information) showed two distinct small structures with a difference in spacing of only a few angstrom, thereby further supporting the presence of this type of hierarchical morphology.

Because of the constant comb density and the perpendicular orientation, with increasing molecular weight, this type of structure would also be expected to remain identical. Room temperature SAXS patterns indeed confirm the formation of small lamellae ($d = 3.9\text{--}4.0$ nm) on the polymer/amphiphile level in all five supramolecular complexes (**Figure S3**, Supporting Information). Although the stained TEM images (**Figure 3a–e**) clearly reveal the increasing size of the block copolymer lamellae with molecular weight, scattering of a large structure in SAXS was found to be absent (**Figure S3**, Supporting Information). Since both large layers are composed of almost exclusively (crystalline) 3-NDP, a low electron density contrast is likely the reason for this.

Given the high dilution of these systems, it is surprising to see that even the lowest molecular weight block copolymer (P4PA31k-47) was able to form an ordered structure at room temperature, also because in the absence of amphiphilic 3-NDP, the diblock is already closely located to the disordered regime ($\chi N \approx 9$). Although this value suggests this particular copolymer to be in a disordered state ($\chi N < 10.5$), uncertainties that were included in the estimation of χN explain the deviating behavior.^[25] An obvious question would however still be: why does this supramolecular approach allow the formation of such well-ordered structures? In order to achieve a better understanding of the driving forces responsible for this type

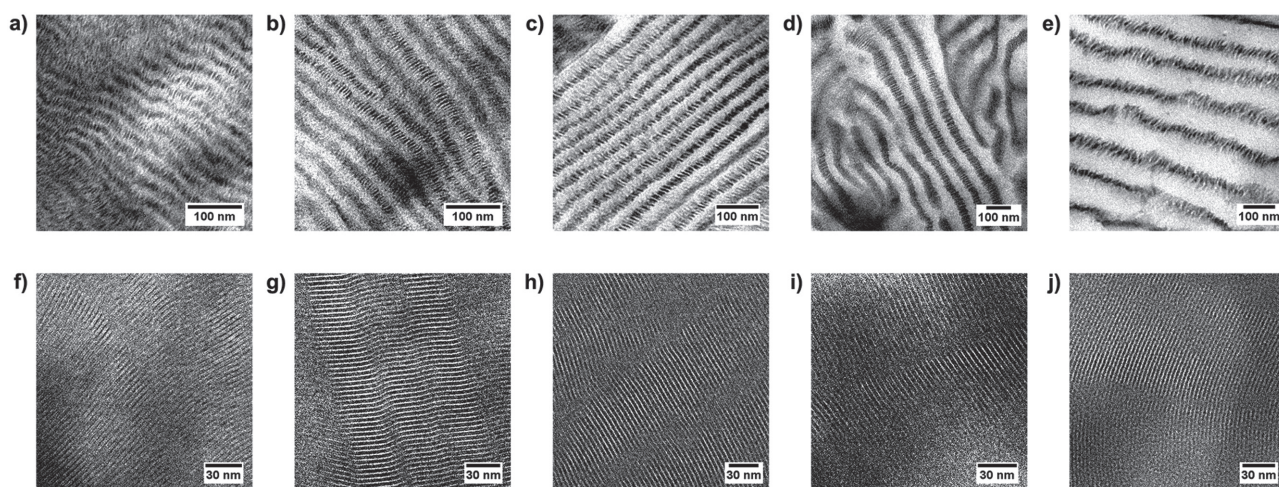
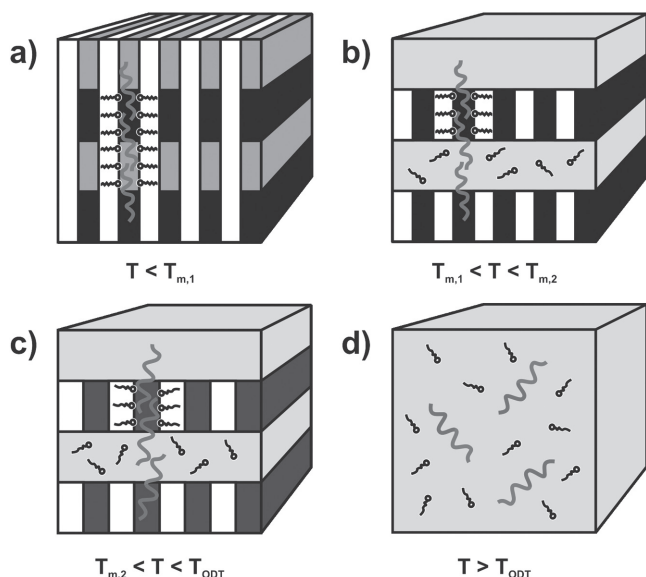


Figure 3. Stained a–e) and unstained f–j) TEM micrographs of P4PA(3-NDP)_{1,0} supramolecular complexes. In the stained images (a–e) P4VP appears dark (iodine vapor). P4PA31k-47 (a, f), P4PA57k-47 (b, g), P4PA109k-48 (c, h), P4PA189k-50 (d, i), and P4PA272k-51 (e, j).



Scheme 2. Schematic representation of the transitions observed in P4PA(3-NDP)_{1.0}. a) Structures at $T < T_{m,1}$ (double lamellae-in-lamellae), b) $T_{m,1} < T < T_{m,2}$ (PAPI(3-NDP) comb disordered), c) $T_{m,2} < T < T_{ODT}$ (liquid crystalline, slightly expanded P4VP(3-NDP) comb), and d) $T > T_{ODT}$ (fully disordered system). Red (P4VP); green (PAPI).

of phase behavior, all complexes were investigated by temperature-resolved SAXS.^[27,28] Taking P4PA109k-48(3-NDP)_{1.0} as an example, scattering as a function of temperature is provided in Figure S4a (Supporting Information) with all phase transitions being highlighted in **Figure 4a**. On heating, the scattering intensity of the small structure ($q = 1.6 \text{ nm}^{-1}$) reduced in intensity around 50°C ($T_{m,1} < T < T_{m,2}$) due to melting of 3-NDP on the PAPI side. On further heating (60°C , $T_{m,2} < T < T_{ODT}$), the crystalline to liquid crystalline transition^[29] of P4VP(3-NDP) caused

this scattering maximum to shift to $q = 1.5 \text{ nm}^{-1}$ ($d = 4.1 \text{ nm}$). In this liquid crystalline state, 3-NDP amphiphiles are no longer crystallized, but still bound to the P4VP polymer backbone, causing a slightly expanded lamellar microphase-separated morphology. The small structure finally disappeared at 70°C , i.e., above the order–disorder transition ($T > T_{ODT}$). The thermal behavior of the homopolymer complexes supports our view on the transitions observed in the double-comb diblock copolymers (Figure S5, Supporting Information). Unlike P4VP(3-NDP), an additional crystalline to liquid crystalline transition was not identified in PAPI(3-NDP); its self-assembly turned out to be crystallization driven.^[23]

Interestingly though, a large structure did appear shortly at $T_{m,1} < T < T_{m,2}$ ($q = 0.0841 \text{ nm}^{-1}$, $d_L = 74.7 \text{ nm}$) (Figure 4a). In between these phase transitions, the self-assembled structure comprises alternating crystalline P4VP(3-NDP)/disordered amorphous PAPI(3-NDP) layers, giving rise to the enhanced contrast in SAXS. Besides that, the absence of any scattering maxima in the patterns at temperatures above T_{ODT} indicates a disordered melt. As all transition are fully reversible (a full cooling/heating scan is provided in Figure S4b in the Supporting Information), the formation of a double-layered morphology can be understood in the opposite direction, i.e., on cooling from a disordered melt. Phase transitions are summarized schematically in Scheme 2. Identical behavior was identified in the other complexes (Figure S6, Supporting Information). Scattering of their large length scale at $T_{m,1} < T < T_{m,2}$ (Figure 4b) can provide an indication of the sizes of the large lamellar structure. Exact numbers are given in Table S2 (Supporting Information). The long period d_L was found to scale as $M_n^{0.62}$ (Figure S7, Supporting Information), which differs significantly from the linear relationship characteristic for true bottlebrush diblock copolymers. Nevertheless, one should be careful with interpretation of this data set, as the measured long period represents a comb-coil system in which PAPI is only swollen by 3-NDP

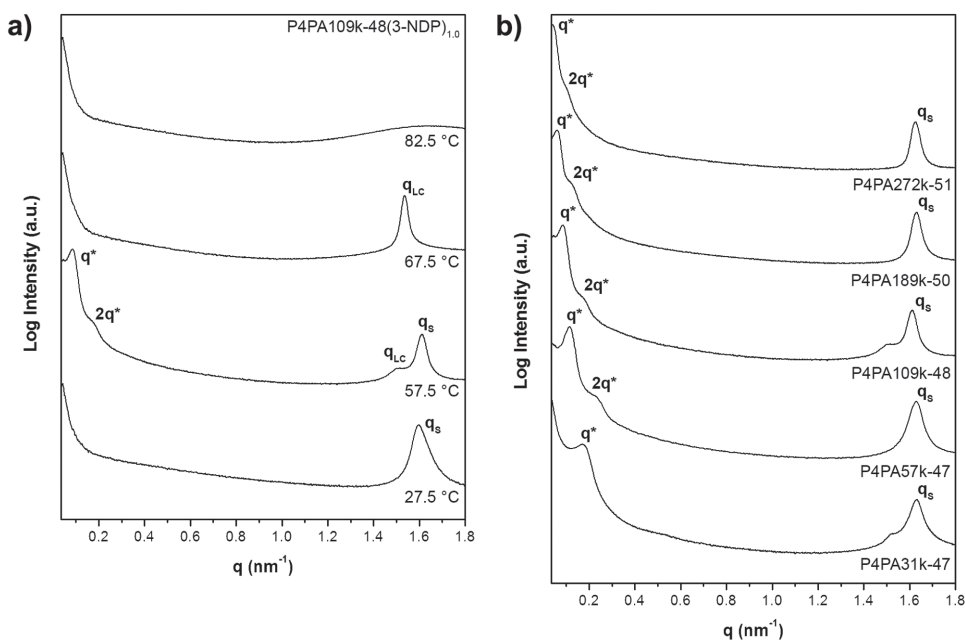


Figure 4. a) Temperature-dependent SAXS profiles of P4PA109k-48(3-NDP)_{1.0}. b) SAXS patterns of P4PA(3-NDP)_{1.0} at $T_{m,1} < T < T_{m,2}$.

(Scheme 2b), thereby likely giving rise to a reduced size of the lamellar structure and a different scaling behavior.^[30]

The presence of a disordered melt is supported by our previous attempt to align the lamellae by shear-induced alignment (P4PA57k-47).^[23] Enhanced ordering was only obtained at $T_{m,2} < T < T_{ODT}$ (a fluid, but microphase-separated state), whereas shear alignment at $T > T_{ODT}$ was unsuccessful. Furthermore, rapid cooling of P4PA109k-48(3-NDP)_{1.0} from $T > T_{ODT}$ resulted in a highly disordered structure (Figure S8 (breakout),^[31] Supporting Information), while a short thermal treatment at $T_{m,2} < T < T_{ODT}$ of ≈ 1 h gave rise to the double perpendicular lamellar-in-lamellar morphology as depicted in Figure 3c. Such a thermal treatment was, however, not necessary for the two lowest molecular weight complexes (P4PA31k-47 and P4PA57k-47), because these double-combs are apparently sufficiently mobile during crystallization of 3-NDP's side chains.

The crystalline nature of both combs and their sequential crystallization thus highly affected the ability to form an ordered morphology, similar to self-assembly of semicrystalline^[32] and double-crystalline block copolymers,^[33] while the liquid crystalline P4VP(3-NDP) block at $T_{m,2} < T < T_{ODT}$ allowed thermal treatment and orientation of the large structure at temperatures as low as 60 °C. Remarkably, the double supramolecular route even worked in low-molecular-weight complexes (i.e., P4PA31k-47). Besides facilitating self-assembly of high-molecular-weight copolymers (e.g., for photonic crystals), this approach could therefore also be interesting to generate sub-10 nm structures for nanolithography using diblock copolymers that would otherwise be disordered in their neat, uncomplexed state. Inclusion of small molecule additives has in certain cases indeed been shown to increase the effective segregation strength.^[34,35]

To summarize, we have shown that the combination of two relatively simple components, i.e., a linear diblock copolymer and 3-NDP surfactants, allows easy design of bottlebrush-like macromolecular architectures, thereby avoiding complicated synthesis routes. Regardless of the molecular weight of the parent diblock copolymer, double perpendicular lamellae-in-lamellae were identified in all high comb density complexes. Furthermore, morphologies were found to be fully thermally reversible and required a 1 h thermal treatment at most. Multiple phase transitions as observed in these highly diluted P4PA(3-NDP)_{1.0} double-combs were found to be responsible for the ability to self-assemble at the block copolymer length scale, even in weakly segregated complexes. Besides very interesting from a fundamental point of view, their highly plasticized nature in the liquid crystalline state could make such double-comb diblock copolymers a very powerful tool for generating well-ordered structures with large dimensions.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

double-comb diblock copolymers, morphologies, order–disorder transition, supramolecular interactions, surface active molecules

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